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Cyclometalated Rhodium Complexes of Phenyl- and Diphenyl-Substituted Oxazole and Thiazole Luminophores

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Abstract—Cyclometaleted rhodium complexes of oxazole and thiazole luminophores [Rh(C^N)$_2$En]Cl [(C^N)$^-$, deprotonated forms of 2,5-diphenyloxazole, 2-phenylbenzothiazole, 2-(biphenyl-4-yl)-6-phenylbenzoxazole, and 2-(biphenyl-4-yl)-5-phenyloxazole; En – ethylenediamine] were obtained and characterized by the methods of ^{1}H NMR, IR, and electron absorption and emission spectroscopy. Two cyclometallated ligands in the inner sphere of the complexes are in the *cis*-C,C positions. Cyclometallating of the luminophores results both in a red shift of intraligand π–π*-optical transitions (Δν ~1.2 kK) as compared to free luminophores and in the appearance of a long-wave band (λ_{max} 376–392 nm) of a mixed nature: metal-ligand charge transfer/intraligand transition. Alongside with the internal conversion to a low-energy state of the metal-ligand charge transfer/intraligand transition, the emission degradation of photoexcitation energy results in the intraligand π–π*-fluorescence of the complexes (λ_{max} 390–423 nm) at room temperature.

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Aryl-substituted azoles are effective organic fluorophores used as activating additives in scintillators [1]. One of the methods for modification of their optical properties is cyclometalating leading to the formation of both intraligand optical transitions and intensive long-wave absorption bands of metal-ligand charge transfer and to the significant changes in luminescent characteristics of fluorophores. Unlike fluorescence of aryl-substituted oxazoles in the ultraviolet region of the spectrum, their cyclometalated complexes of Pt(II) and Ir(III) exhibit intensive phosphorescence in the visible region [2, 3], whereas Pd(II) complexes demonstrate phosphorescence at reduced (77 K) temperature [4] and fluorescence at room temperature [5].

The present work shows the results of study of complexes [Rh(C^N)$_2$En]Cl [(C^N)$^-$ are deprotonated forms of 2,5-diphenyloxazole (dpo), 2-(biphenyl-4-yl)-5-phenyloxazole (bpo), 2-phenylbenzothiazole (pbt), and 2-(biphenyl-4-yl)-6-phenylbenzoxazole (bpbo); En is ethylenediamine].

The studies of the ^{1}H NMR and IR spectra of the obtained compounds show that regardless of the nature of luminophores the complexes include three five-membered metal cycles formed with the participation of the donor N atoms and the deprotonated C atom of the phenyl or biphenyl substituent of azole ligands, as well as two imine donor N atoms of ethylenediamine. The metallating of the phenyl or biphenyl substituent

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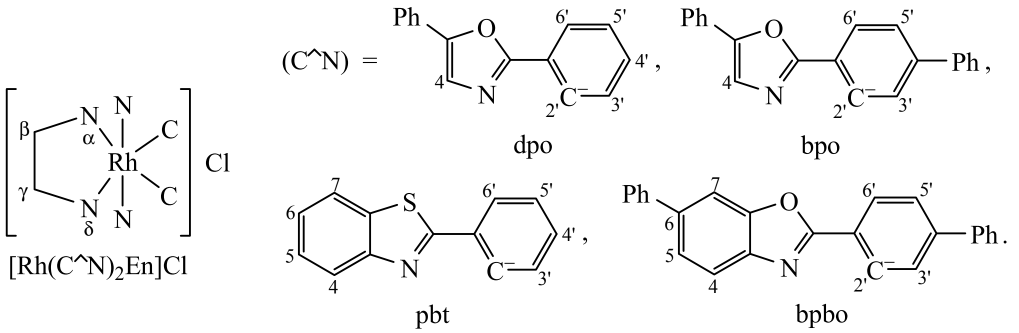

Table 1. Characteristic vibration frequencies (cm^{-1}) of luminophores and complexes

Compound[a]	(C^N)				En	
	ν_{CH} (C_6H_5)	ν_{CH} (C_6H_5)	ν_{CH} (C_6H_5)	ν(C=N)	$\nu_s(NH_2)$	$\nu_{as}(NH_2)$
Hdpo	686, 707, 760, 776	–	–	1609	–	–
[Rh(dpo)$_2$En]Cl	694, 775	735	–	1596	3223	3312
Hbpo	692, 708, 762, 772	834	–	1611	–	–
[Rh(bpo)$_2$En]Cl	690, 711, 747, 769	–	827, 840	1592	3250	3327
Hpbt	686, 759	–	–	1480	–	–
[Rh(pbt)$_2$En]Cl	–	753	–	1474	3291	3352
Hbpbo	691, 701, 764, 773	826	–	1615	–	–
[Rh(bpbo)$_2$En]Cl	697, 762	–	830, 858	1607	3296	3356

[a] Hdpo is 2,5-diphenyloxazole; Hpbt is 2-phenylbenzothiazole; Hbpo is 2-(biphenyl-4-yl)-5-phenyloxazole; Hbpbo is 2-(biphenyl-4-yl)-6-phenylbenzoxazole.

Table 2. Coordination-induced chemical shifts ($\Delta\delta = \delta_{compl} - \delta_{lig}$, ppm) of hydrogen atoms of ligands closest to coordination center in [Rh(C^N)$_2$En]Cl complexes

(C^N)$^-$	4	5	6	7	3'	4'	5'	6'	α	β	γ	δ
dpo	0.8	–	–	–	–1.0	–0.7	–0.6	–0.5	3.1	0.3	0.2	2.7
bpo	0.7	–	–	–	–1.0	–	–0.5	–0.4	3.1	0.4	0.2	2.8
pbt	0.2	0.0	0.0	–0.1	–1.3	–0.8	–0.5	–0.3	3.3	0.4	0.0	2.5
bpbo	0.3	–0.4	–	0.0	–1.0	–	–0.6	–1.1	3.6	0.2	0.2	3.0

of the luminophores leads to the disappearance of the $H^{2'}$ proton resonance from the NMR spectra of the complexes and to the characteristic [6] change of the bands of out-of-plane bending C–H vibrations (Table 1). Two bands of out-of-plane bending C–H vibrations of phenyl-substituted luminophores within the range of 686–776 cm^{-1} are transformed into one band within the range of 735–753 cm^{-1} as a result of the metalating. In case of diphenyl-substituted ligands the metalating of 1,4-disubstituted benzene ring describable by a band within the range of 826–834 cm^{-1} leads to its splitting into two bands at 827–830 and 840–858 cm^{-1}.

The donor-acceptor interactions between Rh(III) and oxazole and thiazole components of luminophores lead to a weak-field displacement of the chemical shift of H^4 protons (Δδ 0.8–0.7 ppm) or of H^5 protons (Δδ 0.3–0.2 ppm) and to the low-frequency shift (Δν 16±3 cm^{-1}) of stretching C=N vibrations (Tables 1 and 2) as compared to free ligands. Spectroscopic ^{1}H NMR and IR characteristics of the phenyl groups of luminophores remote from Rh(III) in the complexes are similar to properties of free ligands.

The coordination of ethylenediamine leads to a displacement of the chemical shifts of amine and ethylene protons to the weak field (Table 2) and to the characteristic (ν_s 345.8 + 0.876ν_{as}) frequencies [6] of symmetric (ν_s 3223–3296 cm^{-1}) and antisymmetric (ν_{as} 3312–3356 cm^{-1}) stretching vibrations of the ethylenediamine N–H bonds (Table 1). A modification of the cyclometalated ligand nature in the [Rh(C^N)$_2$En]Cl complexes owing to the introduction of the fused benzene ring into the heterocyclic component of the ligand results in a simultaneous increase in the chemical shifts of amine protons and frequencies of stretching N–H vibrations of ethylenediamine.

The presence of the hexafluorophosphate ion in the outer sphere of the complex [Rh(pbt)$_2$En]PF$_6$ is charac-terized by the frequencies [6] of bending (ν_4 554 cm^{-1}) and stretching (ν_3 838 cm^{-1}) vibrations.

The mutual anisotropic action of circular currents of two metalated phenyl rings of heterocyclic ligands in the complexes leading to a significant (Δδ –1.0–1.3 ppm) displacement of the chemical shift of $H^{3'}$ protons to the strong field points to the *cis*-C,C-position of cyclometalated ligands in the inner sphere of Rh(III) complexes. In accordance with the *cis*-position of amine protons of ethylenediamine and azole components of heterocyclic ligands, the introduction of the phenyl substituent instead of biphenyl-4-yl into position 2 negligibly affects the difference in chemical shifts of H^{α} and H^{δ} protons of ethylenediamine (Δδ 0.33–0.31 ppm). At the same time, the use of a fused benzene cycle in the azole component of ligands results in an increasing difference in their chemical shifts (Δδ 0.60–0.78 ppm) and in doublet splitting of H^{α} protons (^2J ~11 Hz) (Fig. 1).

The comparison of the electronic absorption spectra of the complexes [Rh(C^N)$_2$En]Cl and free luminophores H(C^N) demonstrate (Fig. 2) that alongside with red shifted (~1.2 kK) intraligand π–π*-optical transitions in the region of <340 nm the cyclometalated complexes are characterized (Table 3) by a long-wave absorption band ($\lambda_{\max}$ 376–392 nm). The results of quantum chemical calculations for Rh(III) cyclometalated complexes [7] point to the mixed $d_{\mathrm{Rh}}/\pi_{(\mathrm{C^\wedge N})}$ nature of the highest occupied molecular orbital (HOMO) and prevailing localization of the lowest unoccupied molecular orbital (LUMO) on the oxazole component of the ligand. This fact makes it possible to assign the long-wave band in the absorption spectra of the complexes to the optical transition of a mixed nature: metal-ligand charge transfer/intraligand transition within the framework of the localized molecular orbital model [8]. In accordance with the mixed nature of the long-wave absorption band of Rh(III) complexes, a decrease in the contribution of the $\pi_{(\mathrm{C^\wedge N})}$ orbital to the HOMO composition leads to a red shift of the long-wave band of Ir(III) complexes by ~2700 kK [3].

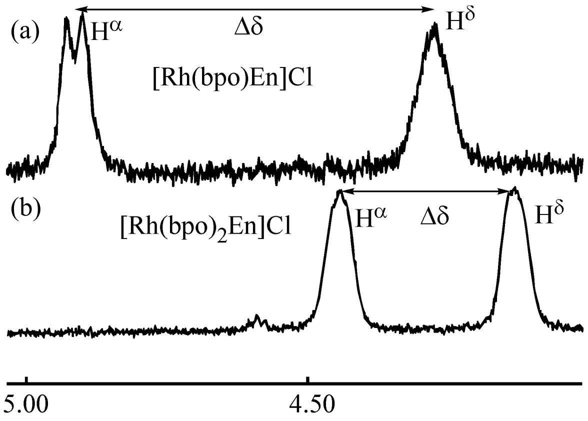

Fig. 1. Fragments of ^{1}H NMR spectrum of complexes (a) [Rh(bpbo)$_2$En]Cl and (b) [Rh(bpo)$_2$En]Cl.

Like free luminophores, photoexcitation of solutions of the complexes at room temperature gives rise to their fluorescence (Fig. 2). The comparison of relative intensity and energy position of fluorescence bands for the complexes and free luminophores show that cyclometalating leads to a more than ~10-fold decrease in the intensity and to a red [2.3–0.5 kK] shift of the fluorescence band. The fluorescence excitation spectra of the complexes are in line (Fig. 2) with their absorption spectra within the range of intraligand bands. However, photoexcitation in a more low-energy region of metal-ligand charge transfer/intraligand optical transition causes no fluorescence. This fact makes it possible to assign fluorescence of the complexes to emission degradation of photoexcitation energy resulting from the intraligand π–π*-optical transition. The decrease in the intensity of fluorescence of cyclometaleted rhodium luminophores as compared to free luminophores appears to be related to a process competing with emissive deactivation of the intra-

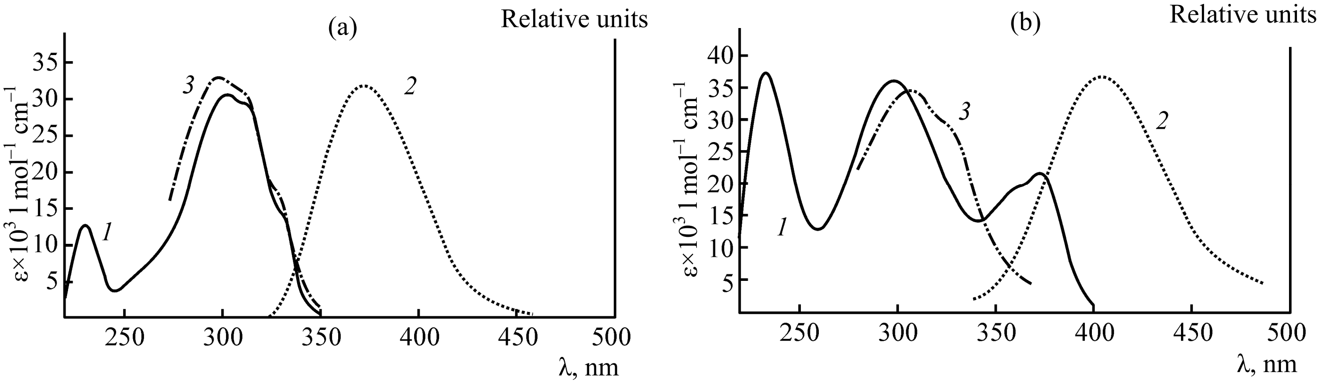

Fig. 2. Spectra: (*1*) electronic absorption, (*2*) fluorescence, (*3*) fluorescence excitation of (a) Hdpo and (b) [Rh(dpo)$_2$En]Cl (CH$_3$CN, 293 K).

Table 3. Optical characteristics of luminophores and complexes (293 K, CH_3CN)

Compound	Absorption λ_{max}, nm ($\varepsilon\times10^3$, l mol^{-1} cm^{-1})	Fluorescence λ_{max}, nm	
		emission	excitation
Hdpo	229 (12.7), 304 (30.8), 316 sh (29), 333 sh (13)	364	299, 314 sh
$[Rh(dpo)_2En]Cl$	230 (35.6), 295 (35.8), 321 sh (24), 361 sh (20), 376 (21.1)	398	287 sh, 312, 330
Hpbt	227 (39.8), 248 sh (17), 255 (16.6), 298 (35.4)	365	289 sh, 299, 309 sh
$[Rh(bt)_2En]PF_6$	227 (46.9), 266 (21.0), 278 sh (20.6), 318 (35.1), 400 (12.6)	390	292, 298, 310 sh, 348
Hbpo	228 (18.8), 260 (16), 322 (51.5), 350 sh (23.2)	392	260, 312, 328
$[Rh(bpo)_2En]Cl$	233 (20.9), 270 sh (16), 303 (19.9), 331 sh (18), 385 (13.6)	399	289 sh, 299, 309 sh, 342
Hbpbo	272 sh (17.0), 326 (60.4)	398	298 sh, 312, 328
$[Rh(bpbo)_2En]Cl$	231 (32.9), 276 (23.9), 317 (35.6), 337 sh (31.7), 392 (16.1)	423	287 sh, 301, 311, 329

ligand π–π*-electron-excited state of the complexes, namely the process of internal conversion into a more low-energy state of metal-ligand charge transfer/intraligand transition. The absence of luminescence of Rh(III) complexes from the state of metal-ligand charge transfer/intraligand transition at room temperature is connected with thermally activated population of *d*–*d*-states subjected to nonradiative deactivation [9, 10].

Thus, unlike cyclometaleted iridium oxazole and thiazole luminophores [3] exhibiting intensive phosphorescence at room temperature from the state of metal-ligand charge transfer/intraligand transition, similar Rh(III) complexes exhibit fluorescence from the intraligand π–π*-state.

The results of the present work demonstrate that preparation cyclometalated rhodium comlexes of phenyl-, diphenyl-substituted, and benzene-fusede azole fluorophores occur to form five-membered {Rh(C^N)} cycles with *cis*-C,C arrangement of two cyclometalated ligands in the inner sphere of the complexes $[Rh(C^\wedge N)_2En]^+$. Optical properties of the complexes are characterized by the presence of both a long-wave optical metal-ligand charge transfer/intraligand transition and a red shift of intraligand absorption bands and also by weak intraligand fluorescence at room temperature.

EXPERIMENTAL

The ^1H NMR spectra, electronic absorption spectra, fluorescence, and fluorescence excitation spectra were obtained at JNM-ECX400A, SF-2000, and Fluorat Panorama spectrometers at 293 K for solutions in $(CD_3)SO$, CH_2Cl_2, and CH_3CN. The IR spectra in KBr tablets were taken on a Shimadzu IR Prestige-21 spectrometer.

The synthesis of 2-phenylbenzothiazole was carried out according to the procedure [11].

Rh(III) complexes were obtained according to the modified procedure [5]. The boiling of 1 mmol of $RhCl_3\cdot3H_2O$ with 2.3 mmol of heterocyclic ligands in the medium of 2-methoxyethanol led to the precipitation of the complex $[Rh(C^\wedge N)_2(\mu\text{-}Cl)]_2$. The addition of ethylenediamine to dimeric complexes suspended in 2-methoxymethanol led to the dissolution of the precipitate due to the reaction of replacement of bridging chloride ligands. The precipitation of the complexes $[Rh(C^\wedge N)_2En]Cl$ from 2-methoxymethanol solution was performed by adding ether, whereas the complexes $[Rh(pbt)_2En]PF_6$ were obtained as a result of KPF_6 precipitation.

Bis[2-(phenyl-2-ido)-5-phenyloxazole] ethylenediaminerhodium(III) chloride, $[Rh(dpo)_2En]Cl$. Yield 41%. ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm (*J*, Hz): 8.68 s (H^4), 7.87 d. d ($2H^{Ph}$, ^3J 8.5, ^4J 1.9), 7.63 t ($2H^{Ph}$, ^3J 7.9), 7.56 d ($H^{6'}$, ^3J 8.0), 7.51 t (H^{Ph}, ^3J 7.5), 6.98 t. d ($H^{5'}$, ^3J 7.3, ^4J 1.1), 6.92 t. d ($H^{4'}$, ^3J 7.4, ^4J 1.5), 6.60 d ($H^{3'}$, ^3J 7.5), 4.37 m ($2H^{\alpha}$), 4.04 m ($2H^{\delta}$), 2.81 m ($2H^{\beta}$), 2.64 m ($2H^{\gamma}$).

Bis[2-(biphenyl-4-yl-3-ido)-5-phenyloxazole] ethylene-diaminerhodium(III) chloride, $[Rh(bpo)_2En]Cl$. Yield 52%. ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm (*J*, Hz): 8.56 s (H^4), 7.90 d ($2H^{Ph}$, ^3J 8.4), 7.78 d ($H^{6'}$, ^3J 7.9), 7.64 d. d ($2H^{Ph}$, ^3J 8.0, 7.5), 7.52 t (H^{Ph}, ^3J 7.4), 7.37–7.25 m ($6H^{Ph',5'}$), 6.82 s ($H^{3'}$), 4.45 m ($2H^{\alpha}$), 4.14 m ($2H^{\delta}$), 2.83 m ($2H^{\beta}$), 2.72 m ($2H^{\gamma}$).

Bis[2-(biphenyl-4-yl-3-ido)-6-phenylbenzoxazole] ethylenediaminerhodium(III) chloride, [Rh(bpbo)En]Cl. Yield 56%. ^{1}H NMR spectrum [(CD$_3$)$_2$SO], δ, ppm (*J*, Hz): 8.29 d (2H^8, ^3J 1.4), 8.17 d (2H^4, ^3J 8.3), 7.90 d (2H^{Ph}, ^3J 8.0), 7.85 d (2H$^{6'}$, ^3J 7.4), 7.55 d. d (2H^{Ph}, ^3J 7.4, 7.5), 7.45 d. d (2H^{Ph}, ^3J 7.3, 7.5), 7.32 d. d (2H^5, ^3J 8.4, ^4J 1.5), 7.22 m (6H$^{5',Ph'}$), 6.81 d (2H$^{3'}$, ^4J 0.4), 4.88 d (2H$^\alpha$, ^2J 10.5), 4.28 m (2H$^\delta$), 2.72 d (2H$^\beta$, ^2J 10.5), 2.69 d (2H$^\gamma$, ^2J 12.3).

Bis[2-(phenyl-2-ido)benzothiazole] ethylenediaminerhodium(III) hexafluorophosphate, [Rh(pbt)$_2$En]PF$_6$. Yield 48%. ^{1}H NMR spectrum [(CD$_3$)$_2$SO], δ, ppm (*J*, Hz): 8.34 m (2H^4), 7.96 m (2H^7), 7.82 d. d (2H$^{6'}$, ^3J 7.6, ^4J 1.1), 7.60 m (4H^{5,6}), 6.99 t. d (2H$^{5'}$, ^3J 7.5, ^4J 1.0), 6.82 t. d (2H$^{4'}$, ^3J 7.5, ^4J 1.3), 6.31 d (2H$^{3'}$, ^3J 7.6), 4.62 d (2H$^\alpha$, ^2J 11.6), 3.84 d (2H$^\delta$, ^2J 7.0), 2.88 m (2H$^\beta$), ~2.5 m (2H$^\gamma$).

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